PHASE TRANSITION STUDIES IN PZT CERAMICS USING ACOUSTIC EMISSION

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Key words: Acoustic emission, Piezoelectric Ceramics, Phase transition and Depoling.

Abstract

Acoustic Emission (AE) – a recent nondestructive testing tool has been used to monitor the acoustic signals, from the widely used hard and soft varieties of lead zirconate titanate - PZT ceramics in the temperature range of ambient to 400ºC. AE signals were observed at the phase transition (PT) temperature during both increasing and decreasing temperature cycles. AE signals were also observed below and above the PT. An un-supervised pattern recognition of the AE signals obtained in these studies has essentially yielded two clusters of signals, indicative of two source mechanisms. The signals at PT are attributed to the micro deformations taking place in the grains due to depoling- in the increasing temperature cycle, and to the structural change from cubic to tetragonal in the decreasing temperature cycle. Depoling and thermal anisotropic contraction of c & a axis, seemed to be the reason for the signals observed below the PT while the few signals observed above the PT were attributed to micro-cracking due to local thermal inhomogeneities. The depoling signals fell under one cluster while the signals due to thermal effects and the signals at about PT while cooling, were found to fall into another category. The differences observed among the PZT varieties, vis-à-vis the AE during these temperature studies are explained. The results were supported by SEM micro photographs. It is suggested that the AE technique when used with pattern recognition (cluster analysis) offers a very simple tool, for in-situ monitoring of the depoling and the phase transition in the above ceramics apart from discriminating the source mechanisms.

Introduction:

Acoustic Emission (AE) is defined as a transient elastic wave generated by the rapid release of energy within a material. All the different processes, which emit elastic waves, act as sources of AE. These are plastic deformation, phase transformation, friction mechanisms, crack initiation and crack growth. When a material is stressed, the externally supplied energy is first stored in the form of strain in the material and when this strain energy reaches a critical level, a redistribution of energy in the form of a dislocation movement or creation or propagation of a micro-crack takes place. During this redistribution, a fraction of energy is converted into acoustic energy, which is emitted from the region where redistribution took place. A good source of information on acoustic emission is a recent book authored by Holroyd [1].

The very first report of work on AE in ferroelectric crystals is by Buchman [2] who reported that stress waves at ultrasonic frequencies are produced in $BaTiO_3$ single crystal as it is heated through its curie point. Lambson et al [3] studied AE from Rochelle salt and TGS crystals during phase transition. The source of AE was presumed to be the lattice structural change around phase transition inducing micro deformations. Dulkin et al [4] studied sound emissions from $BaTiO_3$ crystals near phase transition. A polarising microscope was used to observe the in-situ domain structure. It was found that the main contribution for AE signals came from internal mechanical stresses which appeared in the crystal when the twin structure was modified in the ferroelectric phase several Kelvin below the curie point. The signals were found to be strong during cooling. Mohamed et al [5] studied AE from domain wall motion in ferroelectric lead germinate crystals. They opined that the AE observed is due to domain wall collapse and nucleation and only during the initial forward growth process but not during the sideways motion of domain walls.

Piezoelectric ceramics are much more widely used when compared with single crystals. Srikanth and Subbarao [6] studied AE from ferroelectric lead titanate ceramics. They observed AE at curie temperature (while cooling the specimen) due to sudden change in lattice parameters. AE was also observed below the transition due to anisotropic thermal expansion.

Aparna [7] and Aparna et al [8] studied acoustic emission during phase transition in some soft and hard PZT ceramics, using for the first time waveforms and pattern recognition of these signals, to identify the AE source mechanisms. They observed typical high frequency acoustic emission (HF-AE) signals with principal frequency component around 320 KHz, in the temperature range of about 100 to 250 ºC and a very weak HF-AE signal at phase transition temperature for a poled PZT-5A ceramic sample, during the temperature increasing cycle (T_{INC}). The first lot of AE signals were attributed to the depoling or domain fallbacks, which in turn induce micro-deformations in grains. The AE signal observed at PT was attributed to the structural change from tetragonal to cubic. In the temperature decreasing cycle (T_{DEC}), a typical low frequency acoustic emission (LF-AE) signal observed at PT was attributed to the stresses involved in structural change from cubic to tetragonal leading to microcracking. However, they did not find any such high or low frequency AE signal at PT (both during T_{INC} and T_{DEC} cycles) in other types of PZT ceramics namely 5H, 5J, 4 and 8. Thus the present study is undertaken to understand the absence of AE signals during PT in the PZT ceramics studied by the above workers.

Experimental:

Thickness poled and silver electroded circular disk samples of PZT-5A, PZT 5J, PZT 5H, PZT 4 and PZT 8 (20 mm dia and 1 mm thick), under the trade name of SP5A, SP5J, SP5H, SP4 and SP8 respectively, obtained from Sparkler Ceramics, Pune, India, were used in the present studies. The experimental arrangement to monitor AE from the sample under test is shown in fig.1. The sample which was held in a special holder was kept inside an oven whose temperature was increased from ambient temperature to 400 ^{0}C at an approximate rate of 60 ^{0}C / Hr and later air cooled to bring the temperature down. The temperature of the sample was monitored using a chromel-alumel thermocouple placed inside the brass cup but not touching any of the surfaces (to avoid any unwanted AE signals being recorded). The capacitance of the sample was constantly monitored using a digital LCR meter (Model No. PLCR 8C, Pacific Electronics, Hyderabad, India). The necessary dielectric constant values were obtained from these capacitance readings. Further, the acoustic signals emanating from the sample are conveyed to a wide band AE transducer (175 KHz - 1000 KHz, micro 80D – Physical Acoustics Corpn. (PAC), USA) kept in acoustic contact with an aluminum waveguide of 48 cm length and 5.5 mm dia. The other end of the waveguide is in point contact with the sample under study. The output of the sensor, after 60 dB amplification in a PAC-1220A pre-amplifier, is given to one of the four channels of a DiSP Card (PCI - DiSP, PAC, USA) which has been installed inside a Pentium-IV based Personal Computer. The AE signals were captured at a maximum sampling rate of 10 Mega Samples per Second using the AEWin software (PAC, USA). As the output background noise level was 22mV, the threshold level for capturing AE was set at 31 mV. AE signals were also visually observed throughout the experiment by means of a CRO (model No. IE-522, International Electronics, Bombay, India). For applying the DC field across the sample, a high voltage function generator cum amplifier (Model No. 609E-6-FG, M/s Trek Inc., USA) was used in amplifier mode and an external variable dc of 0 to 3 volts was applied at its input terminals. The output of the thermocouple (temperature) was given as parametric input to the DiSP card for continuous monitoring. The AE setup was acoustically isolated from the surroundings. The experimental data was offline analysed using Noesis, a Pattern Recognition Software.

For a given variety of PZT, two samples from the same batch were experimented. One, for which temperature and capacitance of the sample were continuously monitored, without applying any field, during T_{INC} & T_{DEC} cycles of temperature. For the second sample, temperature and AE signals were continuously monitored from 30ºC to 400ºC, with electric field being applied during a certain range of temperature encompassing the PT. The AE signals obtained at different temperatures from the 2nd sample were plotted as points on a smooth graph showing the variation of dielectric constant with temperature, obtained from the 1st sample. It was assumed that the bulk property like dielectric constant and its variation with temperature could not be different for different samples from the same batch. This method had to be adopted, to avoid any spurious AE signals being recorded due to the connection of the LCR meter across the sample. Also the method of alternatingly capturing AE signals and making capacitance measurement would mean loss of either of the readings (capacitance or AE signal) at the critical PT.

Results, Analysis & Discussion:

Initially, the phase transition study on soft PZT (5A, 5J, 5H) and hard PZT (4 and 8) was performed without applying any electric field, to check the repeatability of the results obtained by the earlier workers (Aparna [7] and Aparna et al [8]) and were found to be same as obtained by them and are summarized below:

1. HF-AE depoling signals were observed mostly between 50º to 200ºC (a typical signal is shown in fig. 2).
2. No AE signals were observed during PT in both T_{INC} and T_{DEC} cycles – except for weak signals in PZT-5A at PT.
3. Some LF-AE signals were observed both below and above PT (a typical signal is show in fig. 3).

The absence of any AE signal at PT both during T_{INC} and T_{DEC} cycles in most of the PZT ceramics studied was found to be puzzling and probably can be explained as given below.

It is very likely that, the sample would be in a fully depoled state by the time it reaches its phase transition temperature i.e. the grains will have net polarisation vectors pointing in random directions. Hence at PT (during T_{INC}) there is no “co-operative” micro-deformation of grains taking place in one single direction due to the structural change from tetragonal to cubic. Therefore, it is reasoned out, that a forced co-operative micro deformations of grains in a single direction would yield AE signals and that these signals should abruptly vanish once the transition is complete. This can be easily achieved by applying a DC field across the sample much before PT (at T_L ºC, where 100ºC < T_L < PT temperature), to orient the net polarisation vectors of the grains in the field direction. This, indeed, yielded result and large amplitude HF-AE signals similar to the ones obtained during depoling (but now they are due to poling and had much larger amplitude than depoling signals) were observed till PT and at PT they abruptly vanished. Few thousands of Ring Down Counts (RDC) were recorded at PT. It was observed that the amplitude of these signals initially increases and then decreases before it vanishes abruptly. Monitoring of AE signals was continued till 400 ºC, but the field was retained till T_H ºC where 400ºC > T_H > PT temperature. Again, during the T_{DEC} cycle the field is reapplied at T_H and was retained till T_L. These two points TL and TH are shown in fig 4. As the sample was cooled during T_{DEC} cycle, large amplitude LF-AE signal was observed at temperature T, where $T_L < T < T_H$. This was indicative of a micro crack being developed in the ceramic due to extensive stresses involved in the structural change from cubic to tetragonal phase. This signal was almost immediately, followed by HF-AE signals indicating domain alignments in the direction of the field. The authors are fully aware of the fact that the field applied itself shifts the temperature at which the PT takes place [9]. After a careful consideration, the electric field to be applied was chosen based upon the fact that it should be sufficiently large and yet not short circuit the sample – neither at PT nor at the highest temperature to which the sample was subjected, nor should it produce any electrical discharge (which will again be an unwanted AE source) in the air across the sample. A detailed account of the experimental conditions and the results obtained in different PZT ceramics studied are given in table -1.

The Initially set threshold value of 31 mV (FIELD OFF) for capturing AE signal was increased to a higher voltage (table-1, column.9), to compensate for the increased noise level introduced by the HV power supply when switched on. It may be noted that typical LF-AE signals were also observed both during T_{INC} and T_{DEC} cycles and at regions below T_L and above T_H.

Fig.4, shows the representative experimental results of the variation of dielectric constant (no field applied) with temperature in the case of SP5A along with the AE signals superimposed (marked as '●'). The thick line around PT in fig. 4 represents a large number of AE signals obtained when the field was applied. For clarity LF-AE signals obtained during the experiment are shown separately in fig. 5. Fig. 6 shows the SEM (FEIXL30 ESEM, Philips) photograph of a microcrack few layers beneath the surface of the positive electrode and perpendicular to the direction of the field applied for the experimented SP 5A sample. Similar such AE results were also obtained in other varieties of PZT samples studied. Any worthwhile differences in results among the samples studied are brought out either in table -1 or in the text below. The experimental results as shown in table -1, fig.4 and fig.5 can be interpreted as follows.

As expected, HF-AE depoling signals were observed in all the samples below T_L during T_{INC}. In the case of SP8 these depoling signals occurred mostly clustered around 75ºC and 230ºC, where as for SP4 these clustered around 60ºC & 225ºC. However, this was not the case in soft ceramics in which HF-

AE depoling signals were observed through out the temperature range of 50 to 250ºC (SP5A), 75 to 100ºC (SP5J), 50 to 150ºC (SP5H). This observation, coupled with the fact that less number of depoling signals were observed in hard ceramics when compared with soft ceramics, support the view that the former are hard to depole.

Barring SP 8 sample, across which electric field could not be applied due to its high conductivity, all the other samples behaved in the way expected during the T_{INC} cycle when the electric field was applied. Large amplitude HF-AE signals due to poling of the sample (domain alignments in the direction of the field) were observed which abruptly stopped at PT (tetragonal to cubic). During the T_{DEC} cycle all the samples across which field was applied – barring SP 5H, gave LF-AE signal (this signal must have been generated by a microcrack - shown in fig. 6 for SP 5A sample due to the stress involved at PT) immediately followed by the sudden appearance of HF-AE signals indicating the PT (now, from cubic to tetragonal).

A simultaneous observation of AE signals on the CRO provided an additional insight especially after the field was applied. It was observed that, with the increasing temperature and with the field applied the background noise slowly starts getting "crowded" and then AE signal is found to build up, cross the threshold, reach a peak value, decrease in amplitude and finally drop down to a value lower than the threshold and merge in to the background noise. The duration for this to happen was found to be few degrees Celsius. Thus, what we perceived as sudden stopping of AE signal at a certain temperature, T_{PT} ºC indicating PT, is the temperature T_A ºC at which the AE signal dies down fully and would be few degrees greater than T_{PT}. Higher the threshold setting, higher would be this (T_A - T_{PT}) ºC. This is evident for SP 5A (table -1) where in which the threshold was set at 314 mV while the peak value of the background noise was only 176 mV. Thus the actual PT could have occurred few degrees higher than 329ºC in T_{INC} cycle and few degrees before (i.e. higher) 316ºC in T_{DEC} cycle. It may be noted that, for all the other samples, (SP 5J, SP 5H, SP4) the threshold was set, just few tens of mV more than the background noise in order to observe the PT more precisely.

It may be noted that the LF-AE signal expected at PT during the T_{DEC} cycle was not noticed in SP 5H. Further studies are being conducted to understand the absence of such a signal.

Fig. 5 shows the temperatures (below T_L and above T_H) at which the other LF-AE signals were obtained in SP 5A sample. These signals are found to occur both in T_{INC} and T_{DEC} cycles of temperature. The number of LF-AE signals during T_{DEC} cycle is greater than those obtained in T_{INC} cycle. To understand the source mechanisms of these LF-AE signals recourse is taken to the 'Learning sets' of signals i.e. signals observed from logically known source mechanisms The authors found the following information quite use full in this regard.

1. While performing the experiments on SP5A samples without field being applied throughout the temperature range (30ºC - 400ºC) – one of the samples (S1) was found to give several LF-AE signals apart from the expected HF-AE depoling signals, as temperature was increasing from 30ºC to 200ºC. The experiment was stopped and the sample was taken for an optical observation at low magnification. This revealed a large number of spots at which the silver electrode got debonded (poled side). Thus debonding of counter electrode could have been the source for some of the observed LF-AE signals.

2. The experiment conducted on yet another sample (S2) – apart from giving the usual AE signals having an amplitude in the range of 30 mV to 3 V, has given very large amplitude (9.7 V) signals, one at 393ºC during T_{INC} and two signals of 10V amplitude at 167ºC and 144ºC during T_{DEC} cycle. Such high amplitude signals would have come only due to a macrocrack. A SEM microphotograph (fig 7) of the sample few layers beneath the surface on the positive electrode side, revealed a large crack parallel to the surface.

Thus, the authors felt that LF-AE signals from S1 and the three LF-AE signals from S2 when taken along with LF-AE signals observed at PT (with the applied field) for SP 5A, SP 5J, and SP 4 and the representative HF-AE signals occurring below T_L and those occurring between T_L and T_{PT} (with the applied field) from SP 5A, SP 5J, SP 5H and SP 4, would yield at least three clusters under an unsupervised pattern recognition analysis (PRA). The result of such PRA using NOESIS is shown in fig. 8., which shows only two clusters using the parameters of zero crossings and average frequency. All the LF-AE signals fell into one cluster and all the HF-AE signals fell into another cluster. It can be seen from the PR chart (fig. 8) the learning signals of debonding (S1) and macro crack (S2) – encompassed by 'O' symbol fell into the same cluster, showing that it is hard to differentiate between debonding and macrocrack signals.

Fig.8, in fact shows several other LF-AE signals occurring below T_L and above T_H (with few representative signals taken from each of the PZT varieties studied). These results point to the fact that the origin of LF-AE signals could be either debonding of counter electrode or microcracking within the specimen. There is a greater chance of debonding signals arising during T_{INC} cycle than during T_{DEC} cycle. This is usually due to the non adherence of the counter electrode to the ceramic sample surface leading to trapping of either gaseous matter or foreign particles (because of uncleaned surface of the ceramic). The expanding gases with increasing temperature will lead to debonding. However, a phase transition study undertaken on an unpoled, uncoated SP 5A ceramic revealed, LF-AE signals both below T_L and above T_H proving that debonding alone is not the source mechanism for the observed AE. Obviously, microcracking seems to be the other source mechanism responsible. It is well known from the literature that microcracking, which is a source of AE, takes place in these PZT ceramics due to internal stresses resulting from incompatible strains between grains during phase transformation, thermal expansion anisotropy or thermal shock [10-12]. Most of these materials have a low overall thermal expansion but possess significant anisotropic axial thermal expansion which causes the micro-cracking and thus the AE. The mode of micro-cracking was found to be mostly inter-granular and propagating along grain boundaries.

Thus the authors feel that thermal anisotropic expansion / contraction could be the reasons for LF-AE signals observed below T_L and higher thermal expansion or thermal inhomoginities between adjacent grains could be the reason for LF-AE signals observed above T_H.

Conclusions:

In conclusion it may be said that, the phase transition can be monitored in PZT ceramics using AE provided an electric field is applied across the sample. A pattern recognition of the observed AE signals revealed two clusters indicating depoling / poling and debonding / microcracking as the two source mechanisms.

Acknowledgements:

Some of the results of the above work have been undertaken in a DRDO sponsored project and the authors thank the concerned authorities. One of the authors, KPR is thankful to DRDO for the award of a JRF. The authors thank the authorities of Osmania University for providing the facilities.

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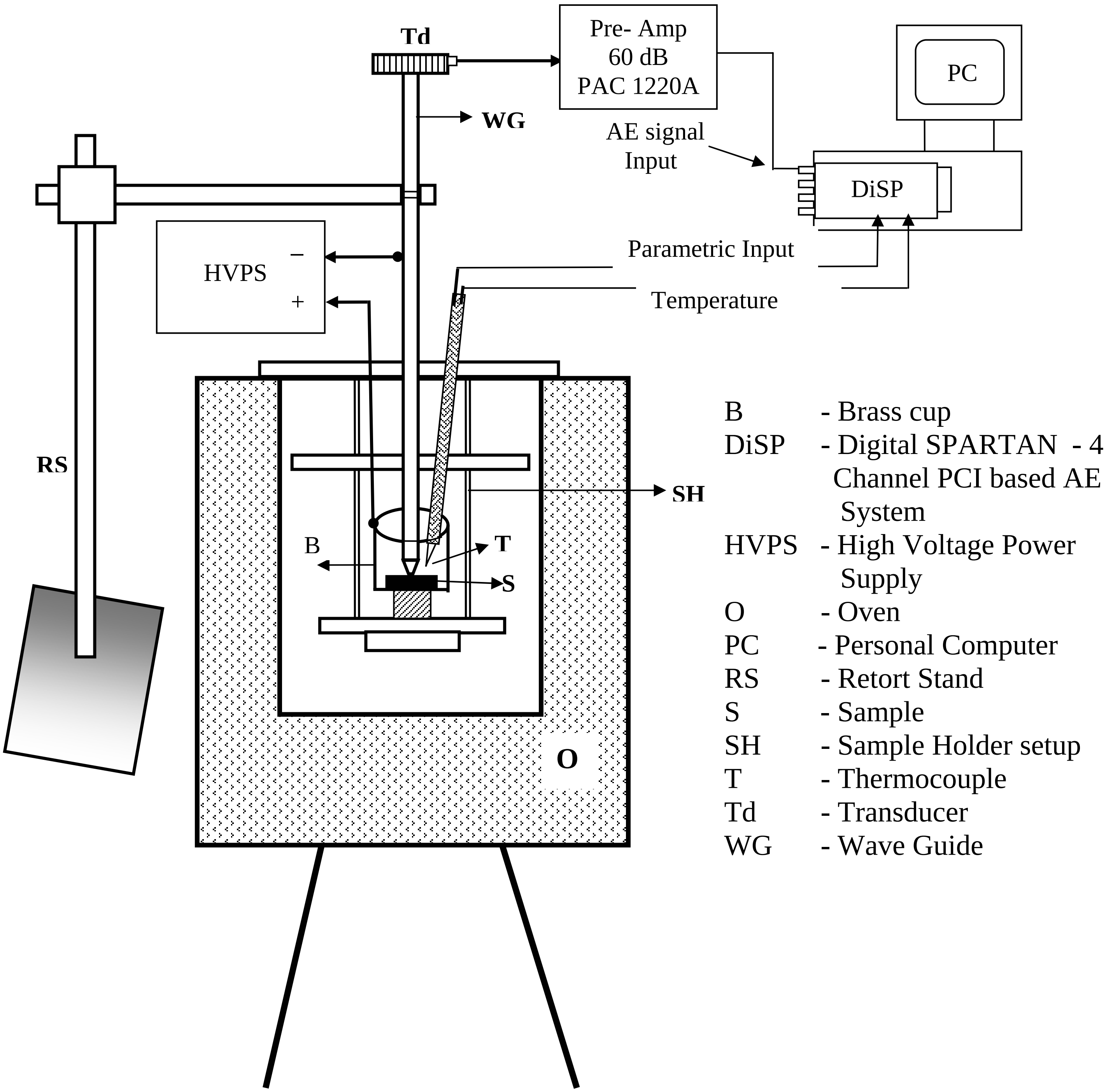

Fig 1. Experimental Setup for Phase Transition studies.

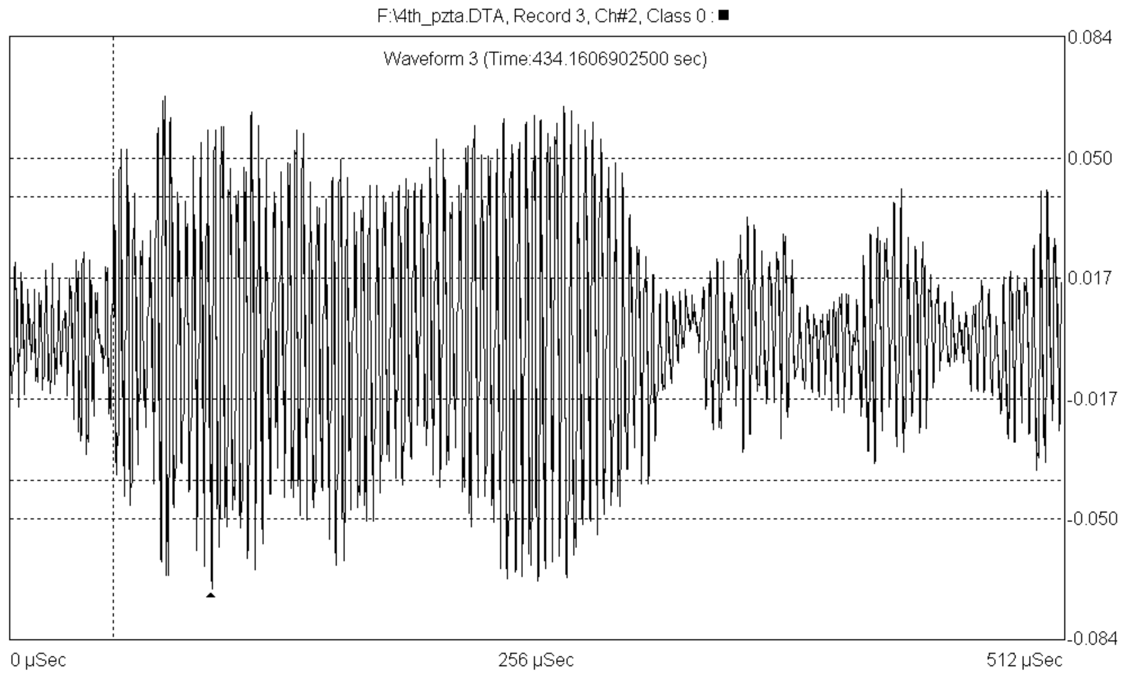

Fig 2 . A typical Depoling (domain fall back) / Poling (domain alignment) Signal.

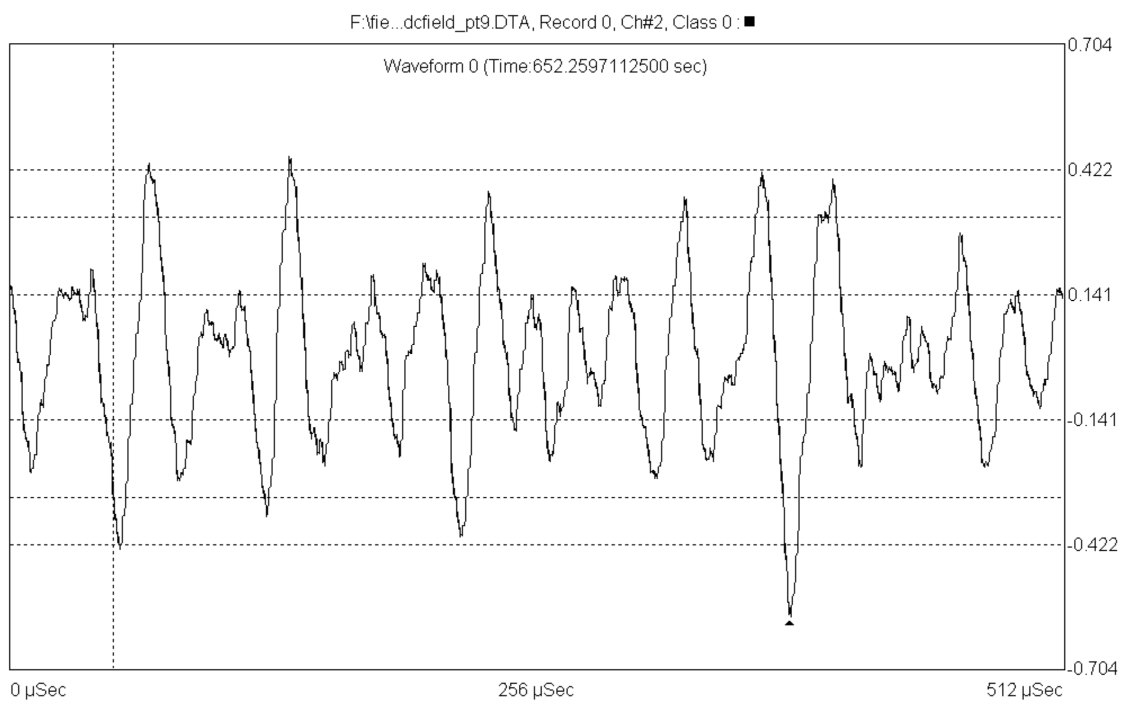

Fig 3. A typical Micro crack Signal obtained at PT (Field ON) during T_{DEC}.

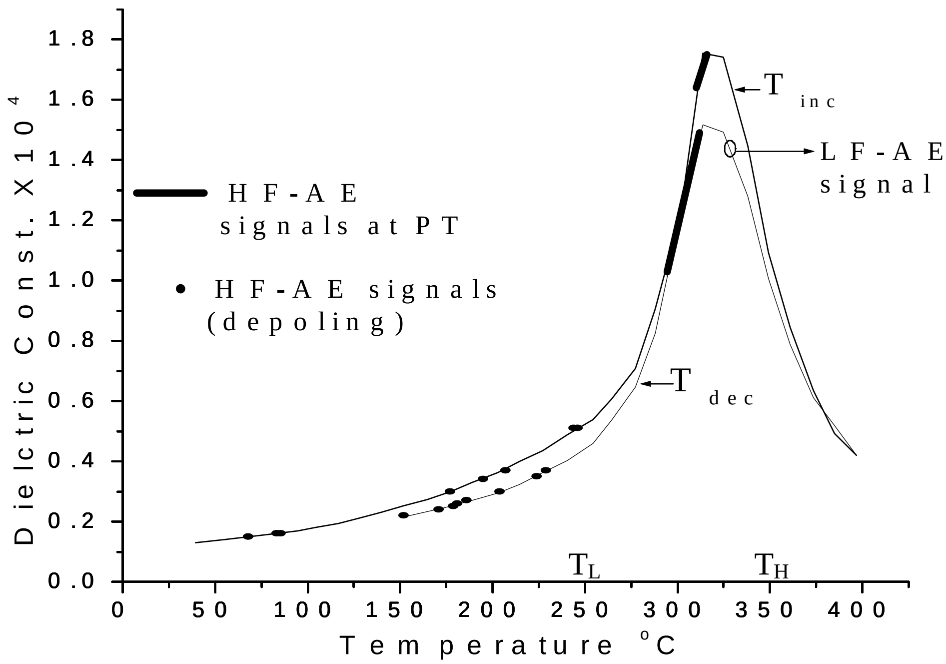

Fig 4. Dielectric Constant Vs Temperature (smooth curve) for SP 5A with HF-AE signals and LF-AE signal at PT superimposed

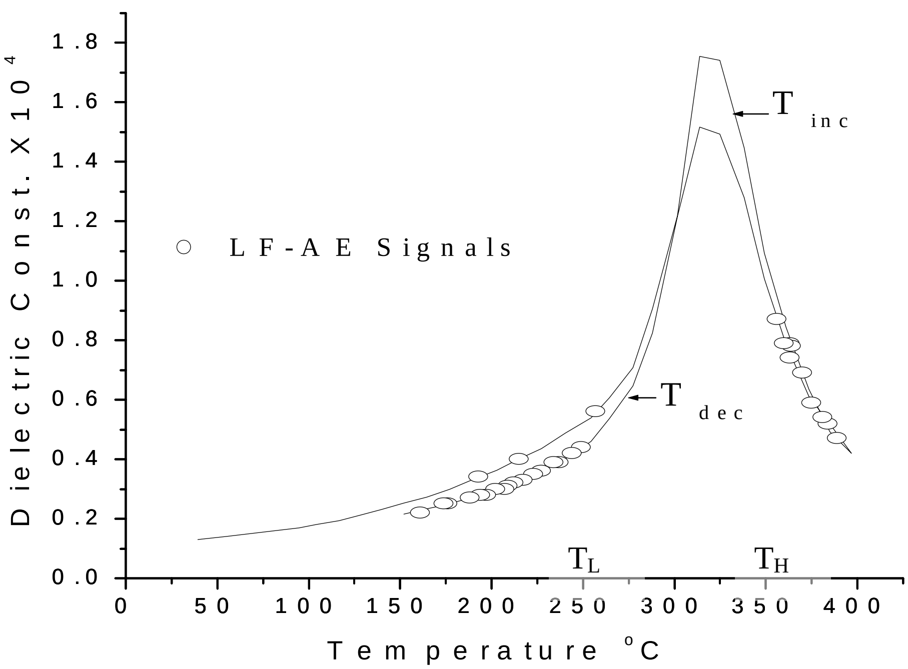

Fig 5. Dielectric Constant Vs Temperature (smooth curve) for SP 5A with LF-AE signals (obtained below T_L and above T_H) superimposed

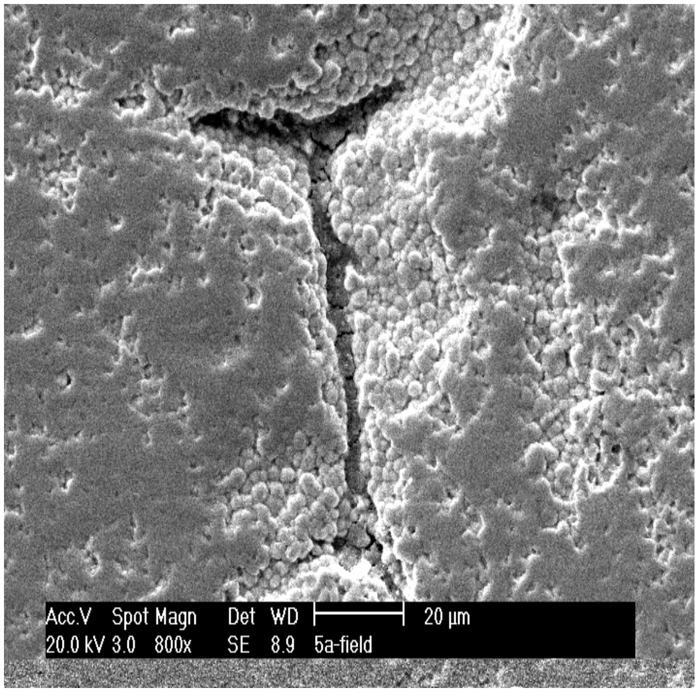

Fig 6. Microphotograph showing the micro crack
in SP 5A (field applied)

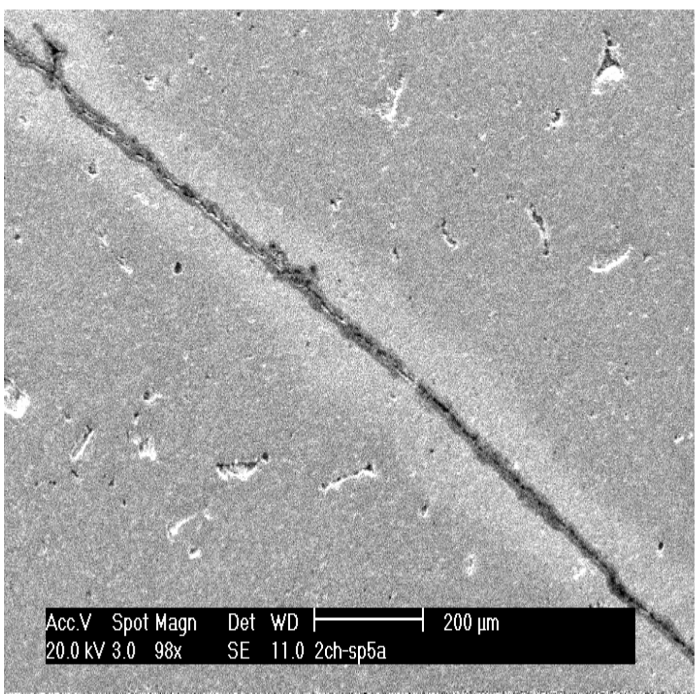

Fig 7. Microphotograph showing a macro crack
in SP 5A (Sample 2 – field not applied)

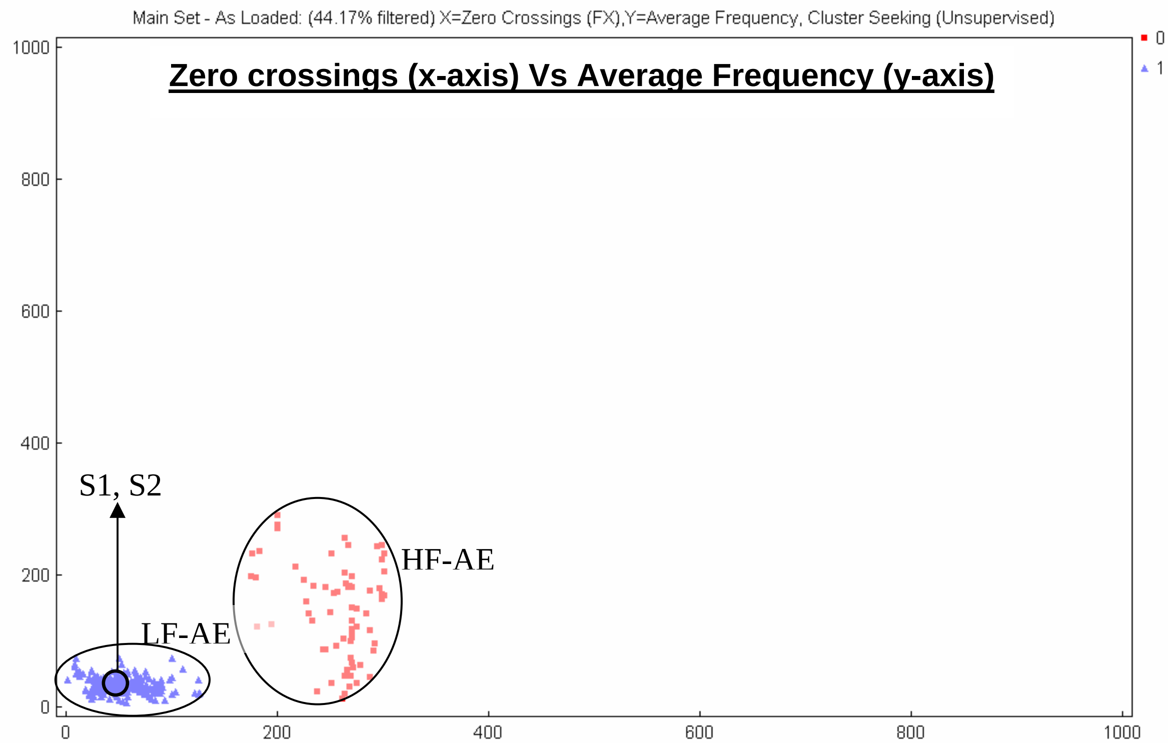

Fig 8. PR chart showing two clusters.

Table 1. phase transition study in different PZT ceramics (Experimental conditions and Results)

Sl. No.	Sample type	Trade name	PT temp. manufac-turer quoted ºC	PT temp. from Dielectric Constant Graph (No field case) ºC	T_L - T_H ºC	Field applied Kv/cm	With FIELD ON: Back-ground noise level mV	New Threshold level mV	Temp. at which HF-AE signals abruptly start in T_{INC} ºC	Temp. at which HF- AE signals abruptly stop while T_{INC} ºC	Temp. at which LF-AE signal is obtained while T_{DEC} ºC
1	PZT 5A	SP 5A	360	315 (314)*	250-350	10	176	314	311	316	329
2	PZT 5J	SP 5J	260	240 (239)	150-300	10	139	176	252	253	254
3	PZT 5H	SP 5H	190	240 (240)	150-275	10	139	176	224.6	229	LF-AE Not observed
4	PZT 4	SP 4	325	332 (331)	250-350	1	250	314	292	270	293.8
5	PZT 8	SP 8	330	311 (306)	---	Nil	22 NO Field	31	---	---	---

Temperature Range of study is from 30 ºC to 400ºC for all the samples

* Value outside and inside the bracket indicates PT temperature during T_{INC} and T_{DEC}